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# *Indian Standard*

## METHODS FOR MEASUREMENT OF AIR POLLUTION

### PART IX OXIDANTS

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MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG  
NEW DELHI 110002

# Indian Standard

## METHODS FOR MEASUREMENT OF AIR POLLUTION

### PART IX OXIDANTS

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*Indian Standard*  
**METHODS FOR MEASUREMENT OF  
AIR POLLUTION**  
**PART IX OXIDANTS**

**0. FOREWORD**

**0.1** This Indian Standard (Part IX) was adopted by the Indian Standards Institution on 26 September 1974, after the draft finalized by the Air Pollution Sectional Committee had been approved by the Chemical Division Council.

**0.2** The oxidants in the atmosphere originate from both man-made and natural sources. Nitrogen oxides and ozone result from air oxidation, electrical discharges and solar radiation. In urban areas fuel burning and auto exhausts contribute significantly to nitrogen dioxide concentration. Chlorine may originate from chemical processes.

**0.2.1** Photochemical oxidants result from a complex series of atmospheric reactions initiated by sunlight. When reactive organic substances and nitrogen oxides accumulate in the atmosphere and are exposed to ultraviolet component of sunlight, the formation of new compounds, including ozone and peroxyacyl nitrates, takes place.

**0.3** In the preparation of this standard, considerable assistance has been derived from ASTM.D 2912-1970 'Standard method of test for content of oxidizing substances in the atmosphere' published by American Society for Testing and Materials, Philadelphia (USA).

**0.4** In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960\*.

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**1. SCOPE**

**1.1** This standard (Part IX) prescribes a method for the determination of low concentrations of ozone plus other oxidants such as nitrogen dioxide, chlorine, peroxyacyl nitrate, etc, which may be present in the atmosphere. It may be used for the manual determination of oxidants in concentrations between 0.01 and 10 ppm as ozone.

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\*Rules for rounding off numerical values (*revised*).

## **2. PRINCIPLE**

**2.1** Micro amounts of ozone and other oxidants are collected by absorption in a solution of potassium iodide buffered to a pH of 6.8. The released iodine equivalent of the concentration of oxidant present in the air is determined spectrophotometrically by measuring the absorption of triiodide ion at 352 nm.

## **3. INTERFERENCES**

**3.1** The method is not specific for ozone since other oxidizing and reducing substances may interfere.

**3.2** Many oxidizing substances besides ozone, will liberate iodine in this method. Nitrogen dioxide, chlorine, peroxy acids, hydroperoxides and peroxyacyl nitrates may also act as oxidants. Reducing gases such as sulphur dioxide and hydrogen sulphide act as negative interferences.

**3.3** Nitrogen dioxide is known to give 10 percent of the response of an equivalent molar concentration of ozone. Nitrogen dioxide reaction occurs as a result of nitrite ion formation in solution. The contribution of the nitrogen dioxide to total oxidant may be estimated by concurrent analysis for nitrogen dioxide

**3.4** The interference from sulphur dioxide is serious. Up to a hundred fold ratio of sulphur dioxide to oxidant may be eliminated by incorporating a chromic acid paper absorber in the sampling train upstream from the bubbler ( absorber ).

## **4. SENSITIVITY**

**4.1** When 10 ml of absorbent solution is used, a range of concentrations between 2 and 20  $\mu\text{g}$  ( 1 to 10  $\mu\text{l}$  ) of ozone corresponds to absorbances between 0.1 and 1 unit in a 1-cm cell. For atmospheric samples containing up to 20 ppm of ozone, linear relationships are obtained between absorbance and sample size.

## **5. APPARATUS**

**5.1 Sampling Probe** — When a sampling probe is used it should consist of glass or stainless steel with a small plug of asbestos, cotton, etc, to screen out particulates and insects. It has been reported that ozone at low concentrations will decompose rapidly upon contact with polyvinyl chloride or rubber tubing. If a rubber tube is used, the sampling probe should be as short as possible and it is best not to sample at too slow a rate.

**5.2 Absorber** — An all-glass bubbler or a bubbler with diffuser may be used for collecting the sample. Bubblers should be kept clean and dust-free. Clean the impinger with chromic acid cleaning solution followed by rinses with tap water and distilled water. Sufficient absorbing solution should be taken in the bubbler.

**5.3 Air Metering Device** — A calibrated flow meter or any device that measures rate or volume with an accuracy of 2 percent may be used to determine the volume of air sampled.

**5.4 Air Pump** — Any pump that will deliver up to about 10 litres of air per minute.

**5.5 Spectrophotometer** — Any suitable spectrophotometer or filter photometer provided with a proper filter (352 nm) is satisfactory. Stoppered cuvettes or tubes suitable for ultraviolet use should be used to hold the solutions.

## 6. REAGENTS

**6.1 Absorbent** — Dissolve 14 g of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), 14.20 g of disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) and 10 g of potassium iodide successively and dilute the mixture to 1 litre with distilled water. Age at room temperature for at least 1 day before use. Measure the pH and adjust to  $6.8 \pm 0.2$  with sodium hydroxide or potassium dihydrogen phosphate solution. This absorbing solution may be stored for several weeks in a glass stoppered brown bottle in the refrigerator and for shorter periods at room temperature without deterioration. The absorbing solution should not be exposed to sunlight.

**6.2 Standard Iodine Solution** — Dissolve 16 g of potassium iodide and 3.173 g of iodine successively and dilute the mixture with distilled water to exactly 500 ml to make a 0.05 N solution. Age at room temperature at least one day before use.

## 7. SAMPLING

**7.1** Assemble a train consisting of a U-tube with chromium trioxide paper (if presence of sulphur dioxide is expected, its interference may be eliminated, *see* Appendix A), bubbler, flowmeter or air metering device and pump. Use ground-glass connections upstream from the impinger.

**7.2** Pipette exactly 10 ml of the absorbing solution into the bubbler and sample at a rate of 0.5 to 3 litres/min for up to 30 minutes. The flow rate and time of sampling should be adjusted to obtain a sufficiently large concentration of oxidant in the absorbing solution. Approximately 2  $\mu\text{g}$  of ozone may be obtained in the absorbing solution at an atmospheric concentration of 0.01 ppm by sampling for 30 minutes at 3 litres/min.

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**7.3** At higher concentrations the sampling time and rate may be reduced so as to keep the absorbance of the solution within the range of the instrument. ( The method is not adopted to concentrations much in excess of 10 ppm. )

**7.4** The total volume of the air sample collected should be corrected to standard conditions of 25°C and 760 mmHg if temperature and pressure deviate appreciably from these conditions. Do not expose the absorbing solution to sunlight.

NOTE 1 — When ozone in the ppm range in air is passed through two impingers in series very little iodine will be liberated from the solution in the second impinger. However, the use of bubblers with diffusers, which have equally high sampling efficiencies, nevertheless results in less iodine liberation for a given amount of ozone. Therefore bubblers with diffusers should not be used in sampling for ozone and other oxidants.

NOTE 2 — The efficiency of collection of the bubbler or bubbler with diffuser for oxidants should be determined by connecting at least one more absorber in series and by estimating the iodine liberated in each of them. The calculated efficiency should be used to correct the results.

## **8. CALIBRATION**

**8.1** Prepare a 0.0025 N iodine solution by pipetting exactly 5 ml of the 0.05 N standard solution ( normality should be checked before use ) into a 100 ml volumetric flask and diluting to the mark with absorbing solution. Prepare four or more standard solutions in 25 ml volumetric flasks by pipetting 0.1 to 1 ml portions of the 0.0025 N iodine solution into the flasks, diluting to the mark with absorbing solution and mixing. Immediately after preparation of this series, read the absorbance of each at 352 nm. The solutions should cover the 0.1 to 1 unit absorbance range.

## **9. PROCEDURE**

**9.1** If significant evaporation of solution occurs, add double distilled water to bring the liquid volume to 10 ml. Read the absorbance at 352 nm against double distilled water within a 30 to 60-minute period after collection in a 1-cm cuvette or tube. Ozone liberates iodine through both a fast and a slow set of reactions. Some of the organic oxidants also have been shown to cause slow formation of iodine. Some indication of the presence of such oxidants and of gradual fading due to reductants may be obtained by taking several readings during an extended period of time. Determine the blank correction (to be subtracted from sample absorbance) every few days by reading the absorbance of unexposed reagent.

## **10. CALCULATIONS**

**10.1** Subtract the absorbance of the blank from the absorbance of the standards. Plot corrected absorbances against the normalities of the

standardized solutions. From the line of the best fit the normality corresponding to an absorbance of exactly one shall be determined. To obtain a value,  $M$ , representing microlitres of ozone required by 10 ml of absorbing solution to produce an absorbance of one, multiply this normality by the factor  $1.224 \times 10^5$ .

**10.2** For 1-cm cells,  $M$  should be approximately 9.6. Results for air samples may be computed from equation:

$$\text{Oxidant (as O}_3\text{), ppm} = AM/V$$

where

$A$  = corrected absorbance, and

$V$  = volume of air sample (in litres) per 10 ml of absorbing solution corrected to 25°C and 760 mmHg (correction is ordinarily small and may be omitted).

**NOTE** — 1 mg/litre = 509 ppm of ozone at 25°C and 760 mmHg.

## APPENDIX A

( Clause 7.1 )

### REMOVAL OF SULPHUR DIOXIDE

**A-1.** Elimination of the interference caused by sulphur dioxide, even if it is present in as high as 100-fold ratio to oxidant, is accomplished by incorporating an extra large (70-ml) absorbing U-tube in the sampling train upstream from the impinger. The absorbent which removes sulphur dioxide without loss of oxidant, is glass fibre filter paper (usual commercial form which has been flash-fired to free it from organic binder) impregnated with chromium trioxide. Add 7.5 ml of aqueous solution containing 1.25 g of chromium trioxide and 0.35 ml concentrated sulphuric acid dropwise over 200 cm<sup>2</sup> of paper so that, visually, the solution is uniformly dispersed on the filter. Dry in an oven at 80 to 90°C for 1 hour. Cut the paper into 6 × 12 mm strips each, fold once into a V-shape, pack into the U-tube, and condition by drawing 0.2 ppm ozone through the tube for 1 hour or dry air overnight. The absorbent has a long storage life (at least 1 month), but deteriorates rapidly with use. If it becomes visibly wet from sampling humid air, it shall be dried with dry air, before further use.

**Caution:** Care in filter preparation and use is important, since a poor filter gives zero oxidant results.



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